Bonding in Cementitious Materials with Asphalt-Coated Particles: Part I – The Interfacial Transition Zone

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Abstract

Reclaimed asphalt pavement (RAP), when used as a coarse aggregate, has been shown to reduce bulk concrete strength and modulus. Part I of this study quantifies and compares the interfacial transition zone (ITZ) for mortar with RAP aggregates relative to dolomite aggregates through image analysis of backscattered electron micrographs. The ITZ with RAP aggregates was larger and more porous with less calcium silicate hydrate (C-S-H) and calcium hydroxide (CH) at the asphalt interface compared with dolomite aggregates. The CH morphology was not significantly affected, although the presence of the asphalt layer may be affecting the CH growth. The addition of silica fume reduced the porosity and size of CH particles in the ITZ with RAP, but not sufficiently to be similar to the ITZ of the dolomite mortar. The microstructural changes

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caused by RAP aggregates, primarily the larger, more porous ITZ, provide strong evidence for the observed reduction in concrete strength and modulus.

1. Introduction

Reclaimed asphalt pavement (RAP) has traditionally been used as recycled aggregate in new asphalt pavements, but has also been identified and studied as an aggregate source for concrete [1–7]. Field demonstration projects have proved the viability of RAP as a virgin aggregate replacement in concrete pavements [8–13]. While there is evidence to support that concrete pavements containing a certain percent replacement of RAP aggregates will have suitable flexural load capacity [2], all previous research studies have indicated that inclusion of RAP aggregates will reduce the concrete strength and modulus [1,2,4–7,14–27]. The poor bonding between the cement paste and asphalt-coated aggregates is believed to be the primary mechanism for reducing the concrete strength and modulus [1,22,26], but no studies have explicitly quantified the microstructural differences of this aggregate-paste interface.

The interfacial transition zone (ITZ) is typically regarded as the region, up to about 50 μm thick, surrounding the aggregate and is characterized by its higher porosity, lower density, lower calcium silicate hydrate (C-S-H) content, lower unhydrated (UH) cement content, larger calcium hydroxide (CH) crystals, and higher ettringite content relative to the bulk paste [28,29].

Quantitative characterization of the ITZ can be performed through image analysis of polished epoxy-impregnated sections using the compositional backscattered electron (BSE) mode in a scanning electron microscope (SEM) [30–32], as has been demonstrated through a number of

studies (e.g., [33–44]). Through greyscale thresholding of a compositional BSE micrograph, the ITZ constituents can be quantified, namely porosity, CH, and UH cement. Past research (e.g., [33–44]) has, in general, shown that across the depth of the ITZ starting at the aggregate interface, the porosity decreases and the UH cement increases. The CH content has been shown to decrease [37,45] or remain relatively constant [34,35]. The C-S-H and otherwise generally-labeled hydration products have also been found to remain relatively consistent across the depth of the ITZ [38,39], although one study found that the total CH plus C-S-H content decreased across the depth of the ITZ [46].

Bonding at the cement-aggregate interface is both physical and chemical. Indeed the ITZ is often referred to as the “weak link” in the failure of concrete, which is primarily related to three sources [47,48]: (1) the higher porosity in the ITZ, (2) the larger and preferentially-oriented CH crystals, and (3) the potentially weak cement-aggregate bond. To fully characterize how RAP affects the ITZ, all three of these items need to be evaluated. Part I of this study focuses on the physical bond, namely as related to Items (1) and (2) above, while Part II will focus on the chemical aspects of bonding, namely Item (3) above.

Investigations of the ITZ properties in concrete with RAP have not been specifically investigated, although Sachet et al. [49] used SEM with secondary electron imaging to examine fracture surfaces of roller-compacted concrete samples with RAP and noted some potential evidence of poor bonding between the asphalt and the cement matrix. The objective of the present study was to examine the microstructure of cement mortars with RAP aggregates with

BSE microscopy in order to quantify how the ITZ composition and morphology are affected by the asphalt coated aggregate particles.

2. Materials and Methods

2.1 Cementitious Mortar

Mortar was prepared consisting of 40% aggregate and 60% cement paste (Type I portland cement with water-to-cement ratio of 0.42) by volume. The aggregates were sieved and washed over a #4 (4.75 mm) sieve to remove fines and dust and then air-dried at 50% relative humidity and 23°C. As aggregate gradation has been shown to influence the ITZ (e.g., [40]), the gradation was controlled to include particles sized 4.75 to 9.5 mm. The mortar was cast in 5 cm by 10 cm cylindrical molds, cured for 24 hours, and then stored in lime-saturated water at 23°C until the necessary age. In the silica fume mortars, 10% undensified silica fume was used as a partial replacement (by volume) of cement. The portland cement composition was primarily 63.0% CaO, 20.7% SiO₂, 5.0% Al₂O₃, 3.2% Fe₂O₃, 2.6% MgO, 2.4% SO₃, 0.5% K₂O, 0.3% TiO₂, and 0.1% Na₂O₃ [50].

Three different RAP sources were investigated in addition to a virgin dolomite aggregate. The three RAP aggregate sources shown in Table 1 consisted of dolomite or steel furnace slag (SFS) aggregates. The effects of these specific RAP sources on the concrete bulk properties were studied previously [1,50,51] along with percent of the aggregates coated with asphalt [52], which are also included in Table 1. The original asphalt performance grade (PG) and the aged asphalt

PG grade is also shown in Table 1. Both RAP1 and RAP2 were sourced from dense-graded asphalt pavement mixtures, with RAP2 being a similar but less processed version of RAP1. RAP3 was milled from the surface layer of an asphalt pavement, which contained SFS to improve abrasion and friction.

Table 1. RAP Aggregate and Concrete Properties

Name	RAP1	RAP2	RAP3
Source Aggregate	Dolomite	Dolomite	SFS*, Dolomite
Asphalt Content	2.10%	3.30%	3.90%
Percent Aggregate Coating	56%	69%	89%
Original Asphalt Grade	PG 70-22	N/A	PG 76-22
Aged RAP Asphalt Grade	PG 88-22	N/A	PG 82-22
<i>28-Day Concrete Strength Properties (MPa)</i>			
0% RAP	46	37	46
20% RAP	37	33	37
35% RAP	33	31	--
50% RAP	28	28	29

*Specifically, this is a basic oxygen furnace slag

2.2 Sample Preparation

The sample preparation methodology and technique in this study was developed based on a number of discussions in the literature [53–58]. After 1, 7, and 28 days of curing, thin sections (~1 mm thick) of mortar were cut with a low-speed diamond saw using isopropyl alcohol as a lubricant. The thin slices were vacuum-dried for 24 hours prior to epoxy impregnation. As asphalt is very susceptible to solvents, solvent replacement techniques were not applicable for

this material, which is why vacuum-drying was employed. Each section measured 15-20 mm by 15-20 mm and was cast into a 32 mm diameter epoxy puck. A low viscosity epoxy (with a measured viscosity of 330 cP) was used to impregnate the samples. The epoxy viscosity was reduced by 50% (330 cP to 160 cP) with the addition of 5% toluene, which has been shown to improve penetration depths in cementitious samples [43].

After 24 hours of curing, the epoxy-impregnated samples were polished for SEM investigation. Successively finer grits of silicon carbide (SiC) grinding papers were used (400, 600, 800, 1200, and P4000) in a dry condition followed by diamond paste down to 0.25 μm on a clean glass plate. Additional polishing details for these samples can be referenced elsewhere [59].

The electron microscopy was performed using a JEOL JSM-6060LV SEM. To ensure conduction, the sides of the epoxy were coated with conductive carbon paint and the top surface was sputter-coated with approximately 75 $\text{\AA}$ of gold palladium. An accelerating voltage of 12 keV was used. All images were taken at a magnification of 500x, resulting in an 8-bit greyscale image measuring 960 by 1280 pixels. Each pixel measured approximately 0.2 by 0.2 μm . The contrast and brightness settings were adjusted such that the image clearly showed the relevant features of pores, hydration products, CH, and UH cement.

2.3 Image Analysis

After digitally removing the aggregate from the image, the greyscale image was thresholded to identify pores, CH, UH cement, and hydration products. Greyscale threshold levels were selected

on a per-image basis from the greyscale histogram and image processing. In the past studies, thresholding levels were visually selected for each image [60–63], while other studies have specified a set of threshold levels to identify properties for all images [46,64], which implicitly assumes that the brightness and contrast settings on the microscope remain constant. To deter the potential errors from thresholding, the per-image thresholding levels utilized for this study account for potential changes in the brightness and contrast settings on the microscope. The porosity thresholding was performed following the pore overflow technique by Wong et al. [65], which selects the threshold from the inflection point in the cumulative greyscale histogram, an example of which is shown in Figure 1a. The UH cement was thresholded based on the local minimum in the greyscale histogram after the hydration product peaks [30,60], as seen in Figure 1b. While CH been reportedly difficult to threshold [37,62,66], in this study a sigma noise averaging filter [44,60] was used to sharpen the peaks in the greyscale histogram. The CH peak was identified at early ages (see Figure 1b), and an iterative CH thresholding process was employed at later ages, particularly for the mortar with silica fume. The BSE compositional images were compared before and after thresholding, and the threshold was iteratively adjusted until the images before and after thresholding were in visual agreement. Additional details can be found in Ref. [59].

(a)

(b)

Figure 1. (a) Porosity thresholding based on the pore “overflow” method [65] using the cumulative greyscale histogram, and (b) the greyscale histogram indicating the how the CH and UH cement were thresholded. This example is from the ITZ of a 1-day old mortar.

The thresholded and filtered image (with aggregate removed), shown in Figure 2a, is used to generate binary masks for porosity, UH cement, and CH (Figure 2b-d). Additional morphological image filtering is applied to the CH and UH binary masks to fill in the features and to remove noise [60,67–70]. After thresholding and filtering, the smallest resolvable CH feature is 1 μm , which is in agreement with Glasser [71].

(a)

(b)

Figure 2. (a) The thresholded and filtered image based on the original image (with aggregate removed), from which the binary masks for (b) porosity, (c) UH cement, and (d) CH can be derived. This sample is a 1-day old mortar.

A refined image analysis technique based upon the Euclidean distance mapping (EDM) approach by Wong and Buenfeld [42] was then implemented. This automated method is centered on a nearest-neighbor algorithm, which allows the image analysis to account for the two-dimensional roughness and tortuosity of the interface. For this analysis, EDM was applied out to a distance of 100 μm from the aggregate interface to determine the porosity, UH, and CH contents as a function of distance from the interface. The binary masks are overlaid with the EDM, as is plotted in Figure 3a for porosity. With the known size of each pixel (0.2 μm) and normalizing the image by the brightness greyscale histogram of the EDM [42], the porosity distribution in the ITZ (up to 100 μm) can be plotted (Figure 3b). The same methodology is applied to the UH cement and CH binary masks to determine the distribution of these phases in the ITZ.

Figure 3. (a) The porosity binary mask overlaid with the EDM out to a 100-μm distance and (b) the resultant porosity distribution along the ITZ.

2.4 CH Morphology

Additional image processing was conducted to characterize the morphology of the CH within 100 μm of the interface to determine if the asphalt coating affected the size, shape, or distribution of the CH. This work follows the analysis on CH morphology presented in the literature [72,73]. Using the CH binary mask, the area (number of pixels), location of the centroid, eccentricity, and equivalent circular diameter of each CH object was defined. The location of the CH particle was defined as the minimum distance between the object centroid and the aggregate interface. The equivalent circular diameter (d_{eq}) [74] is defined by the number of pixels defining the object (A) and the size of each pixel (s), which is 0.2 microns per pixel.

$$d_{eq} = s \sqrt{\frac{4}{\pi} A} \quad \text{Eq. 1}$$

The eccentricity (ecc) of the object describes the elliptical equivalent shape of the object as a function of the size of the major (a) and minor (b) axes.

$$ecc = \sqrt{1 - \left(\frac{b}{a}\right)^2} \quad \text{Eq. 2}$$

An object with an eccentricity of 0 is a perfect circle, while an object with an eccentricity of 1 is line segment. The equivalent ellipse of the object is defined as an ellipse with the same second moments as the identified object [75].

2.5 ITZ Size Estimation

The size (width) of the ITZ was estimated based on the statistical changes in the porosity data from all of the images collected. While a number of methods to estimate the size of the ITZ were investigated [59], a statistical z-test was found to provide the best agreement visually. The z-test was performed to determine the distance x from the interface at which the porosity was not statistically different from the bulk. Based on the number of samples at location x (n_x), the number of samples in the assumed bulk matrix (n_b), the standard deviation at location x (s_x), and the standard deviation of the assumed bulk matrix (s_b), a pooled standard error (se_p) can be computed:

$$se_p = \left[\frac{(n_x - 1)s_x^2 + (n_b - 1)s_b^2}{n_x + n_b - 2} \left(\frac{1}{n_x} + \frac{1}{n_b} \right) \right]^{1/2} \quad \text{Eq.3}$$

The z statistic in this formulation considers the difference in the mean porosity content at location x (X_x) and the mean porosity content of the assumed bulk matrix (X_b):

$$z = \frac{X_x - X_b}{se_p} \quad \text{Eq. 4}$$

3. Results and Discussion

3.1 Effect of RAP on the ITZ

Compositional BSE micrographs of mortars with and without RAP are shown in Figure 4. The asphalt layer typically seen in the BSE image consisted of asphalt mastic, which is a combination of asphalt binder mixed with fines (e.g., quartz, dolomite, and/or SFS). Based on the backscatter coefficient, asphalt appears black in the compositional BSE image. The ITZ properties for equivalent mortars with dolomite and the three RAP sources are shown in Figure 5, Figure 6, and Figure 7 at ages of 1, 7, and 28 days, respectively. Each line represents the average detectable phase percentage collected from approximately 50 ITZ images.

At 1 day, the phase distributions between all mortar samples follow similar trends, suggesting an ITZ size of around 30-40 μm , which supports the literature that the 1-day strengths are not very different between mixtures with and without RAP aggregates [23]. At early ages, the weak bulk paste strength dominates as the failure mode rather than the paste-aggregate bond. The 1-day ITZ data (porosity, CH, and UH) in Figure 5 suggests that the ITZ develops similarly for mixtures with and without RAP.

Figure 4. Compositional BSE micrographs of the ITZ of mortar with (a) dolomite and (b) RAP3.

At 7 and 28 days, the ITZ phase contents seen in Figure 6 and Figure 7 suggest that the mortars will have different mechanical properties, as the porosity and CH are more noticeably different between mortars with and without RAP. The porosity is lower in the ITZ for dolomite mortar and the porosity gradient sharply decreases within a few microns from the interface and then reaches a more “constant” or “bulk” value around 30-40 μm . In contrast, the mortars with RAP have a more gradual decrease in porosity, starting with a higher porosity at the interface, and then reaching a “bulk” value around 40-60 μm , indicating that the ITZ size in mortar with RAP is larger compared to dolomite mortar. This is also illustrated in Figure 8, where the ITZ porosity is plotted for different ages and aggregate sources.

Subtracting the porosity, UH, and CH contents from 100%, the C-S-H content in the ITZ can be approximated (note that this estimation calculation includes other hydration products, such as ettringite, and other minor products and does not purely represent C-S-H) [39]. Figure 9 indicates that the C-S-H content is lower in the ITZ for mortar with RAP compared to dolomite and that the C-S-H content for mortar with RAP approaches the C-S-H content for dolomite mortar after

30-50 μm from the aggregate surface. Other studies have also shown that the C-S-H distribution in virgin aggregate ITZs is relatively constant [38,39], which is consistent with the C-S-H behavior of the dolomite mortar in Figure 9. This lower C-S-H content coupled with the higher porosity in the ITZ with RAP aggregate is one main cause for the known reduction in bulk concrete strength and modulus.

In image analysis of BSE micrographs of cement and concrete, the UH content often has the greatest variability [76]. In general, the UH distribution is similar for all mortars at early and later ages. Since the mortars were each made with the same paste volume and the same water-to-cement ratio, it is expected that the UH contents and distributions would be similar, particularly in the “bulk” matrix. The UH contents within about 20-30 μm are similar across all mortars and ages, suggesting that the asphalt layer on the RAP does not affect the UH distribution near the interface. The average UH contents between each mortar mix deviate more from each other in the “bulk” matrix (at $\sim$ 50-100 μm), which is more of an artefact of the imaging and processing, since the UH grains can be significantly large, thereby biasing the analysis at the length scale that was conducted. Conversely, the porosity and CH are smaller features, so at the length scale studied, there is a less variability in the distribution during image processing and analysis.

The CH content and distribution is similar for all mortars at early and later ages in the “bulk” matrix, but at later ages, the CH content near the RAP interface was lower than that for dolomite mortar. There is evidence of the CH growing preferentially at or on the dolomite aggregate interface, which is most evident at 28 days. Similar behavior of CH growing on or at virgin aggregate interfaces has been noted by a number of researchers [37,45,72,77]. Particularly for

carbonate mineral aggregates, such as dolomite or calcite, there is a the possibility that the calcium hydroxide at the interface is reacting to form a calcium carbonate hydrate phase [78], which has been postulated to increase the mechanical strength. The presence of calcium hydroxide at the interface could therefore be an additional reason why concrete with dolomite aggregates exhibits better mechanical properties than concrete with RAP.

The increasing trend in the CH content away from the aggregate interface for the mortars with RAP suggests that the CH is reacting with the asphalt or somehow the asphalt is preventing CH growth. Since CH is known to nucleate preferentially in (capillary) pores and free space [29] and since the ITZ with RAP is more porous, it is expected that there could be a significant amount of CH near the asphalt-ITZ interface. However, there is evidence in the literature to suggest that CH will react or associate with certain molecules or functional groups in the asphalt [79–81], so it is possible that this is the cause of the reduction in detectable CH at and near the interface. There is also evidence that organic compounds can negatively affect the nucleation or growth of CH crystals in cement paste [82–85], so this is another potential cause of the reduction in detectable CH at and near the asphalt-ITZ interface. This concept is further discussed in Section 3.2 with CH morphology analysis.

Figure 5. Detectable porosity, UH, and CH for 1-day mortars with dolomite and RAP.

Figure 6. Detectable porosity, UH, and CH for 7-day mortars with dolomite and RAP.

Figure 7. Detectable porosity, UH, and CH for 28-day mortars with dolomite and RAP.

Figure 8. Detectable porosity evolution over time (1, 7, and 28 days) for mortars with dolomite (left) and RAP1 (right).

Figure 9. Estimated C-S-H content for 28-day mortars with dolomite and RAP.

The effect of silica fume was evaluated for the mortar mix with RAP2, the results of which for porosity, UH, and CH can be seen in Figure 10. As expected, silica fume decreased the porosity,

and the CH content significantly reduced with age, as the silica fume reacts pozzolanically. At later ages (28 days), the porosity in the “bulk” paste (~50-100 μm) is similar between the mortars with and without silica fume. With regard to the size of the ITZ, the addition of silica fume appears to reduce the porosity at later ages, although the porosity within ~30 μm is not as low as the porosity in mortar with dolomite aggregates. The estimated C-S-H content in the ITZ (Figure 9) increased with silica fume and was similar to dolomite mortar after ~10 μm . While silica fume does decrease the porosity and CH in the ITZ in mortars with RAP relative to mortars without silica fume, the ITZ properties are still not equivalent to the ITZ properties with dolomite aggregates, as indicated in Figure 11. This evidence may explain why silica fume has not significantly improved the bulk strength and modulus properties of concrete containing RAP aggregates [22].

Figure 10. Average detectable porosity, UH, and CH for mortar with RAP2 and with (dashed lines) and without (solid lines) silica fume at (a) 1 day, (b) 7 days, and (c) 28 days.

Figure 11. Comparison of average detectable porosity, UH, and CH at 28 days for mortar with dolomite, RAP2, and RAP2 with silica fume.

The size of the ITZ was estimated from the porosity data using a z-test (Equations 3 and 4) and was found to be on the order of 30-50 μm at 28 days (Table 2). The estimated ITZ size agreed well with the visual estimation in which the ITZ size was greater for mortars with RAP. The addition of silica fume to RAP mortar reduced the size of the ITZ to be comparable with dolomite mortar, although, as noted previously, the ITZ of mortar with RAP and silica fume still exhibits a greater amount of porosity relative to dolomite mortar.

The standard error, determined as the standard deviation normalized by the square root of the sample size, of phase content measurements in the ITZ can potentially be on the order 5-10% for data collected from 50-100 images [32], but Crumbie [37] found standard error values less than 2% for phase content measurements in the ITZ of concrete samples when averaging data from 50 images. The average standard error in the phase content measurements within the size of the ITZ is summarized in Table 2. The standard error for all phases measured are $\leq 1.5\%$, which is comparable or better than the values reported in the literature, validating the sample preparation, image resolution, and image analysis utilized in this study.

Table 2. Size of the ITZ and Average Standard Error within the ITZ at 28 days

Mix	No. of Images	Size of the ITZ* (μm)	Average Standard Error (%)		
			Porosity	CH	UH
Dolomite	58	34	0.9	1.0	0.8
RAP1	57	42	1.2	0.6	0.9
RAP2	56	54	1.4	0.7	0.9
RAP2 (with Silica Fume)	53	28	1.3	0.5	0.7
RAP3	55	52	1.5	0.8	0.8

*Determined based on porosity data

Concrete cast with 50% coarse RAP aggregate (specifically the RAP1 source) was shown to reduce compressive strength and elastic modulus around 35-40% and 30%, respectively [1]. If about 56% of the RAP1 particles are coated with asphalt [52] and 50% of the coarse aggregate in the concrete is RAP (which corresponds to about 20% of the concrete volume with about 0.4% of the concrete volume is asphalt), then it can be argued that the larger, more porous ITZ is the primary cause of the reduction in elastic modulus, since the ITZ accounts for around 20-40% of the total concrete volume [29]. Using multi-phase composite models and accounting for the larger ITZ, Brand [59] demonstrated that the reduction in predicted elastic modulus of concrete with RAP agreed with the measured elastic modulus. While asphalt is a lower modulus phase

relative to mineral aggregates and the cementitious matrix, the total volume of the material in the concrete precludes it from being a primary cause of the overall reduction in concrete modulus; in addition, one previous study showed that changing the stiffness of the asphalt by altering the temperature of the concrete did not greatly impact the dynamic modulus of the concrete [1].

Based on these presented data, one question that arises is what is the mechanism causing the larger, more porous ITZ. One consideration is the hydrophobic nature of the asphalt is repelling water from the interface. The water gradient that forms around the aggregates in fresh concrete [47] would therefore be repelled, preventing hydration products from effectively and efficiently packing and growing around the aggregate and resulting in the larger, more porous ITZ.

However, this repelling mechanism is not acting on the order of the ITZ size (i.e., tens of microns), but it is illustrated by the sharp decrease in porosity for dolomite mortar at 7 and 28 days within a few microns of the interface compared to the relatively little decrease in porosity in mortars with RAP over the same distance. An additional concept for the larger, more porous ITZ in RAP mortars concerns the idea that the asphalt is somehow poisoning cement hydration.

Studies in alkaline solutions have indicated that asphalt leachate contains a greater total organic carbon content relative to neutral pH solutions [86,87]. In a pH 13.5 simulated cement solution, qualitative analysis indicated the presence of aromatic, alcohol, aldehyde, glycol, carboxylic acid, and amine compounds in the asphalt leachate [87]. Polycyclic aromatic compounds have also been identified in the leachate [88–90]. While the effect of the majority of these specific compounds on cement hydration has not explicitly been examined, a number of studies have reported that organic compounds can detrimentally affect cement hydration, such as aromatic and other cyclic compounds [84,91,92], alkanolamine and other amine compounds [91,93,94],

and glycol compounds [85,95]. It is therefore plausible that organic compounds are being leached in the high pH pore solution and at least some of these compounds are detrimentally affecting the cement hydration in the ITZ with RAP, as evidenced by the decrease in C-S-H and other hydration products and the increase in porosity. As the ITZ phase distributions are similar for all mixtures at 1 day, this leaching behavior and hydration poisoning effect appears to manifest at later ages.

3.2 CH Morphology

At 7 and 28 days, the mean CH particle size (by equivalent diameter) was found, in general, to be slightly lower for mortar with RAP compared to dolomite, as presented in Table 3. As expected, the addition of silica fume did reduce the mean CH particle size relative to the other mortars. As seen in Figure 12, the distribution of CH particle sizes at 28 days was similar between the various mortars with the exception of the mortar with silica fume, which indicated a greater percentage of smaller particles. The mean particle size calculated was smaller than the values reported by Diamond [72], which was on the order of 7-8 μm , but Diamond ignored all particles smaller than 4 μm , so the mean values are naturally lower in this study as the smallest CH particle size in this analysis was 1 μm .

The CH particle eccentricity was similar between the mortars with and without RAP, as indicated in Table 4. On average, the CH particle shape was much more elliptical than circular, which has been indicated in other studies as well [72,73]. The number of CH particles relative to the interface also does not appear to be greatly affected by the asphalt coating, as shown in

Figure 13, suggesting that CH can and will nucleate near mineral aggregate and asphalt interfaces. For all mortars, it appears that the greatest amount of CH particles is within 20-30 μm , which is expected given the higher porosity within the ITZ.

Figure 13 suggests that the ITZ in mortars with dolomite and RAP have approximately similar amounts of CH particles, whereas the CH content distribution from Figure 7 indicated that dolomite mortar had a greater area (volume) of CH growing very near or on the aggregate interface relative to the mortar with RAP. The 28-day mean particle size at the interface (within 1 μm) are 4.7 μm (dolomite), 4.4 μm (RAP1), 4.5 μm (RAP2), 4.3 μm (RAP3), and 3.7 μm (RAP2 with silica fume). Thus, it can be reasoned that mortar with and without RAP at 28 days have similar amounts of CH particles within the ITZ (i.e., the presence of asphalt does not affect CH nucleation) but that CH appears to preferentially grow at the dolomite aggregate interface and not as much in the presence of asphalt (i.e., the presence of asphalt does affect CH growth). This effect on CH may be a result of the organic compounds leaching from the asphalt, as there is some evidence to support that certain organic compounds can interfere with CH growth [82–85], such as through complexing with Ca^{2+} .

Table 3. Mean Equivalent CH Particle Sizes with Age

Age (days)	Mean Equivalent CH Particle Sizes (μm)				
	Dolomite Mortar	RAP1 Mortar	RAP2 Mortar	RAP3 Mortar	RAP2 Mortar with Silica Fume
7	4.7	4.5	4.6	4.4	4.3
28	4.8	4.5	4.8	4.5	3.9

Figure 12. Histograms of CH equivalent circular particle diameters (within 100 μm of the aggregate interface) for each of the mortars (with and without FRAP) at 28 days.

Table 4. Percent of CH Particles as a Function of Eccentricity at 28 Days

Eccentricity	Percent of Particles (%)				
	Dolomite Mortar	RAP1 Mortar	RAP2 Mortar	RAP3 Mortar	RAP2 Mortar with Silica Fume
0.0	14	15	17	15	17
0.1	0	0	0	0	0
0.2	0	0	0	0	0
0.3	0	0	0	0	0
0.4	1	2	1	2	2
0.5	1	1	1	1	1
0.6	4	5	4	5	4
0.7	9	9	8	9	8
0.8	23	23	23	23	23
0.9	31	31	30	30	31
1.0	16	14	14	14	13

Figure 13. Histograms of CH distance from the aggregate interface (within 100 μm of the aggregate interface) for each of the mortars (with and without RAP) at 28 days.

4. Conclusions

The use of reclaimed asphalt pavement (RAP) as an aggregate in concrete mixtures has been shown to reduce the concrete strength and elastic modulus in multiple studies. The interfacial transition zone (ITZ) between the portland cement mortar with RAP aggregates relative to dolomite aggregates has been hypothesized as one reason for the changes in bulk properties. Polished, epoxy-impregnated samples were prepared and examined using compositional backscattered electron imaging. Image analysis was performed using greyscale thresholding and a Euclidean distance mapping approach to quantify the amounts and distribution of detectable porosity, unhydrated (UH) cement, and calcium hydroxide (CH) as well as CH morphology over time in the ITZ. The average standard error of the phase contents in the ITZ were lower than previous literature, validating that the polishing, resolution of the BSE images, filtering, thresholding, and phase identification techniques were overall improved for this study.

The ITZ properties and phase distributions at 1-day were not very different between mortars with and without RAP. As the ITZ continued to develop, the 7- and 28-day ITZ properties in mortar with RAP had higher porosity, a larger ITZ width, and less CH (and less C-S-H) content at the interface, which can be related to the reductions in concrete strength and modulus. It is hypothesized that the high pH pore solution is leaching organic compounds from the asphalt, which may be poisoning the hydration process, resulting in the greater porosity and less C-S-H in the ITZ and potentially affecting CH growth. The source of the RAP aggregates tested did not impact the ITZ properties. The mean CH particle size and shape were not drastically different between mortars with and without RAP aggregates. All mortars had similar amounts of CH particles, although the mean CH particle size may be smaller near the asphalt (RAP) interface, which suggests that the asphalt is somehow reacting with or hindering the growth (but not the nucleation) of the CH. The addition of silica fume did reduce the porosity in the ITZ of mortar with RAP aggregates, but did not reach the lower ITZ porosity level measured in the mortar with dolomite aggregates. Based on a statistical analysis, the ITZ size for all aggregates was found to range between 30 and 50 μm with the dolomite aggregate ITZ being smaller than the ITZ adjacent to RAP aggregates. Based on these findings, the higher porosity content and larger ITZ width are primary factors that cause reductions in the bulk concrete strength and modulus when RAP aggregates are introduced.

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